(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 328 336 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89301149.4

(22) Date of filing: 07.02.89

(51) Int. Cl.4: B 65 D 81/26

(30) Priority: 10.02.88 GB 8803065

(43) Date of publication of application:
16.08.89 Bulletin 89/33

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: W.R. Grace & Co.-Conn. (a Connecticut corp.)
Grace Plaza 1114 Avenue of the Americas
New York New York 10036 (US)

(72) Inventor: Hofeldt, Robert H.
1 Orchid Drive
Littleton Massachusetts 01460 (US)

White, Steven Andrew Carl
56 Station Road Ivinghoe
Nr.Leighton Buzzard Bedfordshire LU7 9EB (GB)

(74) Representative: Lawrence, Peter Robin Broughton et al
GILL JENNINGS & EVERY 53-64 Chancery Lane
London WC2A 1HN (GB)

(54) Container closures and Materials for use in these.

(57) A preformed container closure element, such as a cap, removable panel or liner, is formed of a polymeric matrix containing an oxygen scavenger. Preferably the scavenging properties of the scavenger are activated by pasteurising or sterilising the element after fitting it to a filled container.

EP 0 328 336 A1

Description

Container Closures and Materials for Use In These

This invention relates to materials that can be used to improve the shelf life of packaged materials, such as bottled beer.

It is standard practice to package food and other materials within laminated polymeric sheet material that generally often includes a barrier layer of low permeability to oxygen. The sheet material can be thin, in which event it is wrapped around the material being packaged, or it can be sufficiently thick that it forms a container body that is provided with a lid or other separate closure. The polymeric sheet material thus constitutes most or all of the exposed surface area of the container.

It is known to include an oxygen scavenger in the sheet material. The oxygen scavenger reacts with oxygen that is trapped in the package or that permeates through the laminate. This is described in, for instance, U.S. 4,536,409 and 4,702,966 and the prior art discussed in those. For instance, U.S. 4,536,409 describes cylindrical containers formed from such sheet material and provided with metal lids.

When the container is formed of a glass or metal body and is provided with a metal closure then permeation of oxygen through the body and the closure is impossible because of the impermeability of the materials from which the body and closure are formed. However it has long been recognised that when conventional containers of this type are used for the storage of materials such as beer, the shelf life of the stored materials is very limited. The quality of the beer tends to deteriorate after storage for a month or so. The only effective way of prolonging the storage life has been to provide a gasket of cork and aluminium foil between the closure and the container body but this is wholly uneconomic. Accordingly at present it is accepted that the shelf life of beer, especially in bottles, is rather limited.

Traditionally the closure was of metal but there is a trend now towards forming the closure of polymeric material.

Even when the body of the jar or bottle is wholly impermeable, e.g., of glass, and the polymeric cap makes an airtight fit with the jar or bottle, possibly through a gasket between the cap and the jar or bottle. it is well accepted that some deterioration of fillings such as beer may occur on storage. Accordingly it is well accepted that, when using polymeric caps for beer and other bottles, it is generally necessary to restrict the shelf life.

It would be very desirable to be able to improve the shelf life significantly whilst continuing to use conventional materials for the formation of the container body, the container closure and the gasket between the body and closure.

According to the invention, a container comprises a container body and a closure comprising a preformed solid element formed of a polymeric matrix containing an oxygen scavenger.

The preformed solid element is preformed in the sense that it is applied to the closure or to the container in a previously manufactured form and shape and is not subsequently altered as by melting or flowing. This is in contrast to the invention described in our copending application (Case 3029) filed even date herewith in which a fluid or molten composition is applied on to a container closure to form, for instance, a solid gasket on that closure.

The closure occupies, as is conventional, only a minor part of the exposed surface of the closed container often less than 25% of the exposed surface area of the container. Thus the area of the solid element can be very small relative to the exposed area of the container. Despite this, the invention can give greatly improved storage stability.

The preformed element may constitute the entire closure or part only of the enclosure. If it is the entire closure, then the closure is normally a cap and the cap is formed of the polymeric matrix containing the oxygen scavenger. The cap can be moulded with an integral seal or intended for use with an inserted disc gasket or with a gasket that is lined on to it from a molten or fluid composition.

If the element constitutes part only of the closure, it can be in the form of a panel that defines part of the closure. For instance the closure can be mainly of metal but can have a removable panel of polymeric material that can be torn out or otherwise ruptured in order to open the container.

Another closure element of the invention is a liner or other preformed disc that is fitted between the neck of the filled container and the remainder of the closure, which can be of metal.

The container body is preferably of metal or glass but can be of polymeric material.

In one preferred aspect of the invention, the container body is of glass or polymeric material (especially being a jar or bottle filled with beer) and the preformed solid element is a plastic cap for the jar or bottle.

The cap may be metal or may be polymeric. Thus it may be formed by, for instance, injection or compression moulding of a suitable thermoplastic composition that may contain, as a thermoplastic polymer, polyethylene, polypropylene, ethylene propylene copolymer, polystyrene, polyacetyl, polyethylene terephthalate or a blend of two or more of these. The composition from which the cap is made may include other conventional ingredients for such compositions, including anti-oxidants, slip aids and fillers, generally all in minor amounts. The oxygen permeability of the cap is often at least 2cc STP/cm/cm^2/sec/cmHg x 10^{10}, often 2 to 5.

In its simplest embodiment, a cap formed of such polymeric material and containing oxygen scavenger is the closure on a jar or bottle of glass or of polymeric material, such as polyethylene terephthalate or any of the other polymers mentioned above. When the body is formed of polymeric material, the oxygen permeability of the body may be substantially zero or may be higher, for instance at least 0.07,

typically 0.07 to 2cc STP/cm/cm^2/sec/cmHg x 10^{10}.

The polymeric cap may be a crown cap, a twist-on cap or a screw cap or any other form of polymeric cap suitable for closing jars and containers.

Instead of or in addition to forming the cap of the polymeric matrix containing oxygen scavenger, the cap or other closure may be provided with an inner liner or other preformed disc or ring of the matrix containing oxygen scavenger. For instance the cap may be provided with a preformed internal disc of polymeric matrix containing oxygen scavenger or a polymeric film of such a matrix may be sealed across the open top of the iar. The disc or ring is introduced in its final form and may be held loosely in the cap or it may be trapped in the cap by appropriate shaping of the inner face of the cap.

This preformed disc or ring may, in some instances, serve as a satisfactory gasket between the closure and the container body. For instance it may be a butyl rubber or other polymeric ring of the type used as a gasket in baby-food jars.

When the disc or ring is not a gasket, then a gasket of polymeric material may be provided between the closure and container body. This gasket may be of conventional material or, as described in copending application (case 3029) the gasket may be formed on the closure from a fluid or meltable composition that comprises polymeric matrix material and oxygen scavenger.

In another type of closure, the container body is usually a can and part of the closure is a removable panel. For instance the main panel of a can end may be of metal whilst a smaller area within the main panel, and defining part of the main panel, may be removable by pulling or pushing and may be of polymeric matrix material. For instance there may be a polymeric pull tab component set within a main metal panel. There may be an inner layer of polymeric material applied over the metal surface, for instance to promote bonding of the removable polymeric panel to it. This inner layer may be formed by depositing a fluid or molten composition over the metal (as described in copending application (case 3029). Preferably, in the invention the removable polymeric panel is formed of the polymeric matrix containing oxygen scavenger. Examples of closures having a removable panel of polymeric material, and to which the invention can be applied, are given in GB 2,180,321, 2,158,383 and 2,158,423 and in EP 153068 and 215671.

Removable panels, preformed discs or other elements for use in the invention may be formed by moulding thermoplastic compositions as discussed above for use in the manufacture of caps.

The essential feature of the invention is that the composition from which the cap and/or other preformed closure element is formed contains an oxygen scavenger, that is to say a reducing agent that can react with gaseous oxygen. The composition may also contain small amounts of anti-oxidant in known manner to stabilise the polymeric composition against degradation due to free radicals caused by reaction between oxygen and the polymer. The scavengers of the invention however react with gaseous oxygen.

The oxygen scavenger is preferably a reducing agent that reacts with gaseous oxygen in an ionic reaction that requires the presence of moisture.

Although the literature, such as U.S. 4,536,409, recommends potassium sulphite as a scavenger we find that it is particularly desirable to use ascorbates or isoascorbates or mixtures thereof with each other or with a sulphite, often sodium sulphite. In general the alkali metal (usually potassium or sodium) salts of sulphites, ascorbates and isoascorbates are preferred. Organic reducing agents such as tannins can be used.

A preferred aspect of the invention is that the scavenger should remain substantially inert in the closure element until the closure is on a sealed container. Generally the polymeric matrix substantially protects the scavenger from moisture under normal atmospheric conditions.

Exposure of the matrix to the high humidity that normally exists within a sealed container may therefore result in sufficient permeation of moisture into the element to give a satisfactory degree of scavenging and improved shelf life. However the scavenging reaction can be accelerated by heating the element to cause increased permeation of moiture. Thus preferably the scavenger is a material that remains substantially inert in the polymeric matrix until the scavenging reaction is triggered by heating in the presence of moisture.

Preferably the scavenging reaction is triggered by pasteurising (typically at 50 - 100°C) or sterilising (typically at 100 - 150°C) the container after filling it with an aqueous fill and sealing it, using the closure element of the invention. This acceleration appears to be a consequence of the composition, when heated, permitting moisture to permeate into the polymeric matrix and to become trapped in the matrix thereby bringing the scavenger into contact with sufficient water to permit reaction with oxygen. This oxygen may permeate through the matrix either from oxygen trapped within the container when it was filled or from the surrounding atmosphere.

In order to maximise the effect of the scavenger on oxygen that is already in the container, it can be desirable for the scavenger to be located internally of a layer of very low permeability. For instance it can be in an inner layer of a laminated polymeric cap having a barrier layer outside the scavenger layer, or it can be an insert disc.

It may be desirable to include in that composition a material, for instance a surfactant such as sodium dodecylbenzene sulphonate, which will increase the permeability of the matrix to water and a suitable amount of a surfactant such as this is between 0.1 and 1.0% by weight.

When the scavenger is in the cap or an insert, the amount of the scavenger is normally at least 1% based on the weight of the cap, generally at least 3% and preferably at least 4%. It is generally unnecessary for the amount to be above 15% and 6% or 8% is often a convenient maximum. Expressed in an alternative manner, the amount of scavenger is typically in the range 0.1 to 3g, often 0.2 to 2g, per cap. Some of this amount may be in a gasket or other inner closure element. When the scavenger is

only in a gasket or other element, the amount may be at least 0.5% based on the polymeric matrix material of that element, generally at least 1.5% and preferably at least 3%. It is generally unnecessary for it to be above 10% and 5% is often a convenient maximum.

It is particularly preferred that the oxygen scavenger is selected from ascorbates, isoascorbates, and tannins, or mixtures of two or more of these or mixtures of one or more of these with a sulphite. The use of such scavengers, in preference to sulphite alone, as is recommended in the literature (such as U.S. 4,536,409) gives beneficial advantages such as more reliable scavenging under variable processing conditions, and is applicable to closures of metal or of polymeric material. The following is an example.

Example 1

A cap-forming composition is formed of polypropylene with 7% sodium ascorbate blended into it. Bottle caps are injection moulded from this composition in conventional manner. When the caps are used for sealing bottles filled with beer, and which are subsequently pasteurised, the beer has a longer shelf life.

Claims

1. A product that comprises a container closure for closing a filled container body, wherein the closure comprises a preformed element of polymeric matrix and is characterised in that the matrix contains oxygen scavenger.

2. A product according to claim 1 in which the preformed element is selected from the entire closure, a removable area defining part of the closure, and a preformed disc that can be fitted between the remainder of the closure and filling in the container body.

3. A product according to claim 1 or claim 2 wherein the container closure is fitted to a filled container body.

4. A product according to claim 3 in which the container body is of metal or glass.

5. A product according to claim 4 in which the closure is of metal and the element is a preformed disc or ring for insertion in the closure or is a removable panel in the closure.

6. A product according to claim 3 in which the container body is of polymeric material.

7. A product according to any preceding claim in which the closure is a polymeric cap formed of a polymeric matrix containing the oxygen scavenger.

8. A product according to claim 7 in which the cap is moulded from polymeric materials selected from polyethylene terephthalate and polypropylene.

9. A product according to any preceding claim in which the oxygen scavenger is a reducing agent that reacts with gaseous oxygen by ionic reaction in the presence of water and is substantially inert in the absence of water.

10. A product according to claim 9 in which the preformed element of polymeric matrix is non-aqueous and the oxygen scavenger in the element is substantially inert to oxygen under normal atmospheric conditions, and in which the scavenger can become scavenging to oxygen upon subjecting the element to heat in the presence of moisture.

11. A product according to any preceding claim in which the amount of oxygen scavenger is from 1 to 10% by weight based on the weight of polymeric matrix material.

12. A product according to any preceding claim in which the oxygen scavenger is selected from sulphites, ascorbates, isoascorbates and tannins.

13. A product according to any preceding claim in which the oxygen scavenger is selected from alkali metal ascorbates or isoascorbates and mixtures of alkali metal ascorbates and/or isoascorbates with alkali metal sulphite.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 1149

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	WO-A-8 001 559 (METAL BOX LTD) * Abstract; page 1, lines 1-4; page 2, line 30 - page 3, line 5; page 5, line 24 - page 6, line 13 *	1-4,6,7,9,11-12	B 65 D 81/26
Y		10,12-13	
A		8	

X	US-A-4 279 350 (KING) * Column 2, lines 12-38; figure 1 *	1-6	
A		7-8	

Y,D	US-A-4 536 409 (AMERICAN CAN CO.) * Claims 67,85 *	10,12	

Y	PATENT ABSTRACTS OF JAPAN, vol. 40, no. 50, 16th April 1980, page 86 C 7; & JP-A-55 22 317 (TAISEI HOUZAI K.K.) 18-02-1980 * Abstract *	13	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

B 65 D
C 12 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-05-1989	BRIDAULT A.A.Y.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)